

United States Patent [19]

Baumann

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[54] PHENOLAMINES

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[58] Field of Search 260/501.21, 501.15, 260/501.16; 564/360, 361, 355

[56] References Cited

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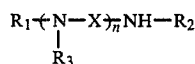
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[57] ABSTRACT

Compounds of formula I



in which

R₁ is an aliphatic C₆₋₂₂ residue

R₂ is an optionally substituted salicyl group

each R₃, independently, is H or an optionally substituted salicyl group

n is 0 or an integer from 1 to 10

each X, independently, is —C₂H₄— or —C₃H₆—

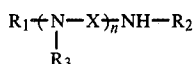
provided that the molecule contains from 1 to 5 optionally substituted salicyl groups in free base, protonized or quaternized form, are useful as dyeing or printing after-treatment agents, particularly to improve the oxidative wet fastness of dyeings or printings on cellulose containing material.

13 Claims, No Drawings

PHENOLAMINES

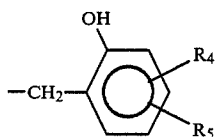
The invention relates to phenolamines, which are useful as dyeing or printing after-treatment agents, particularly to improve the oxidative wet fastness of dyeings or printings on cellulose material.

According to the invention, there is provided a process for after-treating a dyed or printed textile substrate comprising cellulosic fibres, which process comprises bringing the dyed or printed substrate into contact with a compound of formula I



in which

R₁ is an aliphatic C₆₋₂₂ group
R₂ is a group of formula (a)



each R₃, independently, is hydrogen or a group of formula (a)

each R₄, independently, is hydrogen or C₁₋₁₂ alkyl
each R₅, independently, is hydrogen, chlorine, C₁₋₁₂alkyl, cycloalkyl or phenyl

n is 0 or an integer from 1 to 10

each X, independently, is —CH₂H₄— or —C₃H₆— provided that the molecule contains from 1 to 5 groups of formula (a) in free base, protonized or quaternized form.

The aliphatic residue as R₁ may be saturated or unsaturated. It is preferably a linear or branched C₆₋₂₂alkyl or C₆₋₂₂alkenyl group, more preferably C₁₂₋₁₈alkyl or C₁₂₋₁₈alkenyl, particularly cetyl, stearyl or a mixture of C₁₄₋₁₈ alkyl and/or alkenyl derived from reduced natural fatty acids such as tallow fatty acid.

Any alkyl as R₄ or R₅ may be straight or branched chain; alkyl is preferably C₁₋₄alkyl, particularly methyl or ethyl.

Any cycloalkyl as R₅ is preferably cyclohexyl.

When R₄ is alkyl, it is preferably in the ortho or meta position to the hydroxy. When R₅ is other than hydrogen, it is preferably in the para position to the hydroxy. Preferably R₄ and R₅ are each hydrogen.

Preferably the group of formula (a) is salicyl.

When X is —C₃H₆—, it may be linear or branched. n is preferably an integer from 1 to 10. More preferably n is 1, 2, 3 or 4, particularly 3 or 4.

Preferred compounds of formula I are those in which R₁ is C₁₂₋₁₈ alkyl or C₁₂₋₁₈ alkenyl, R₂ is salicyl, each R₃ independently is hydrogen or salicyl, X is —C₃H₆— and n is 1, 2, 3 or 4, the molecule containing 1, 3 or 4 salicyl groups.

Further preferred compounds of formula I are those in which R₁ is cetyl, stearyl or tallow fatty residue, R₂ is salicyl, X is —C₃H₆— and either n is 3 and R₃ is salicyl or n is 4 and one R₃ is hydrogen and the remaining R₃'s are each salicyl.

The nature of the anion of the protonized or quaternized compounds of formula I is not critical. Preferred anions are halogenide, e.g. Cl⁻ or Br⁻, benzenesul-

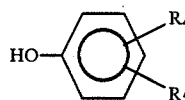
phonate, p-toluenesulphonate, formate, sulphate, methylsulphate or phosphate. More preferred are Cl⁻ and formate, especially Cl⁻.

Compounds of formula I in which n is an integer from 1 to 10, in free base, protonized or quaternized form are novel and form part of the invention.

Compounds of formula I may be prepared by reacting one mol of an amine of formula II



in which R₁, X and n are as defined above, or a mixture thereof, with 1 to n+1 mole formaldehyde and 1 to n+1 mole of a compound of formula III



in which R₄ and R₅ are as defined above, or a mixture of compounds of formula III,

the formaldehyde and the compound of formula III being each reacted in equimolar amounts,

and, where desired, converting the resulting compounds of formula I obtained in free base form into a protonized or quaternized form or vice versa.

The reaction may be carried out according to known methods, e.g. according to a Mannich-condensation.

The resulting compounds of formula I in free base form may be protonized by reaction with an organic or mineral acid, e.g. benzenesulphonic acid, p-toluenesulphonic acid, hydrochloric acid, hydrobromic acid, phosphoric acid etc., or quaternized by reaction with a quaternization agent, e.g. dimethylsulphate, methyl chloride, benzyl chloride etc. Depending on the amount of acid or quaternization agent used, it is possible to protonize or quaternize one, several or all of the basic nitrogen atoms present in the molecule (depending on the value of n).

The compounds of formula I, in free base or in salt form, may be obtained in liquid, pasty or solid form depending on their nature. They may be purified according to known methods.

The compounds of formula I are useful as dyeing or printing after-treatment agents, in particular for after-treating dyeings or printings on cellulose containing textile material to improve their oxidative wet fastness.

Cellulose containing textile material includes substrates which comprise natural and/or regenerated cellulose, preferably cotton. The substrate may be in any conventional form, e.g. yarn, woven or knitted goods, fully finished articles etc.

The compounds of formula I are applied to the textile substrate after dyeing or printing. Dyeing or printing is carried out according to known methods with direct or reactive dyestuffs. After fixation of the dyestuffs the textile substrate is advantageously washed or rinsed.

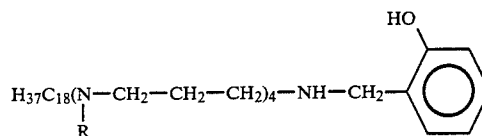
The compounds of formula I may be applied to the dyed or printed textile substrate by known methods, for example by impregnation, e.g. padding, or by the exhaust method. The liquor to goods ratio is suitably from 0.7:1 to 60:1. The application may be effected at a temperature from room temperature to 100° C. In the case of impregnation, fixation is carried out according to known methods, at a temperature from room temperature to approx. 180° C.

The application of the compounds of formula I may be suitably effected at a pH of from 4 to 7. It may then be advantageous to add an alkaline reacting agent, e.g. sodium trichloracetate, to the treatment liquor.

Suitably the treatment liquor contains from 0.1 to 10 g/l of a compound of formula I, preferably from 0.5 to 5 g/l when the compound of formula I is applied by the exhaust method. The padding solutions suitably contain from 1 to 100 g/l, preferably from 10 to 80 g/l, most preferably from 10 to 60 g/l of compound of formula I.

Depending on their solubility in water, the compounds of formula I may be added as such to the treatment liquor or admixed first with a solubilising agent, e.g. a glycol such as ethylene glycol or a glycol monoether, e.g. butyl diethylene glycol or propyl ethylene glycol.

resulting product is, if necessary, adjusted to pH 3. The resulting phenolamine of formula



in which one R is hydrogen and the remaining R's are each salicyl, can be used as such a solution in ethyleneglycol for the after-treatment.

By repeating the procedure of Example 1 but using the amines, phenol and formaldehyde in the amounts indicated in the following Table, further phenolamines of formula I can be produced.

TABLE

Ex. No.	Amine	Moles Phenol	Moles CH ₂ O	converted into salt form with
2	C ₆ H ₁₃ —NH ₂	1	1	1 mol dimethylsulphate
3	C ₁₂ H ₂₅ NH ₂	1	1	1 mol dimethylsulphate
4	tallow fatty (C ₁₄₋₁₈)-amine	1	1	1 mol dimethylsulphate
5	C ₁₈ H ₃₇ —NH—C ₃ H ₆ —NH ₂	1	1	1 mol dimethylsulphate
6	C ₁₈ H ₃₇ —(NH—C ₃ H ₆) ₂ —NH ₂	1	1	1 mol dimethylsulphate
7	"	1	1	1 mol dimethylsulphate
8	C ₁₈ H ₃₇ (NHC ₃ H ₆) ₃ —NH ₂	1	1	1 mol dimethylsulphate
9	"	1	1	1 mol dimethylsulphate
10	C ₁₈ H ₃₇ (NHC ₃ H ₆) ₄ —NH ₂	1	1	1 mol HCOOH
11	"	1	1	1 mol HCL
12	tallow fatty residue-(NHC ₃ H ₆) ₄ —NH ₂	1	1	1 mol dimethylsulphate
13	C ₁₈ H ₃₇ —NHC ₃ H ₆ NHC ₂ H ₄ —NHC ₃ H ₆ NH ₂	1	1	1 mol dimethylsulphate
14	tallow fatty-amine	1	1	free base
15	C ₁₂ H ₂₅ —NHC ₃ H ₆ (NHC ₂ H ₄) ₂ —NHC ₃ H ₆ NH ₂	1	1	1 mol CH ₃ Cl
16	tallow fatty residue-(NHC ₃ H ₆) ₄ —NH ₂	2	2	free base
17	tallow fatty residue-(NHC ₃ H ₆) ₄ —NH ₂	1	1	free base
18	C ₁₈ —H ₃₇ —(NHC ₃ H ₆) ₄ —NH ₂	4	4	1 mol HCL

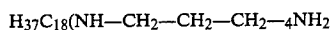
After the treatment with a compound of formula I the textile substrate is dried.

Dyeings or printings after-treated with a compound of formula I have an improved oxidative wet fastness, in particular improved fastness to chlorine water. This fastness property is nowadays of increasing importance since the tap water used for washing has an increasing chlorine content. Swimming pool water also has a high chlorine content. Cellulose dyeings or printings obtained with conventional dyestuffs are sensitive to the deleterious action of chlorine water and this action is even stronger when the goods are washed warm.

The following Examples, in which all parts and percentages are by weight as far as not otherwise indicated, illustrate the invention. The temperatures are given in degrees Centigrade.

EXAMPLE 1

455 Parts amine of formula



and 376 parts phenol are introduced in a flask fitted with a reflux condenser and heated to 90°. 120 Parts paraformaldehyde are then added portionwise to the mixture while stirring and maintaining the temperature below 100°. After 5 hours stirring at 95°–100° the water resulting from the reaction is removed by distillation at 80° under approx. 20 mm Hg. The vacuo is then stopped and the mixture is heated at 85° with vigorous stirring. To this mixture is added first and slowly 341 parts concentrated HCl (pH ≤ 3) and then 978 parts ethyleneglycol. After cooling to approx. 20° while stirring, the

APPLICATION EXAMPLE A

Bleached cotton fabric is dyed at 40° for 90 minutes with an aqueous dyebath containing 1.9% dyestuff C.I. Reactive Red 123 (based on the dry weight of the fabric) and, per 1000 parts, 50 parts calc. sodium sulphate and 20 parts calc. sodium carbonate. The liquor to goods ratio is 20:1.

After dyeing the fabric is thoroughly rinsed with warm and cold water. Thereafter the fabric is soaped at the boil for 20 minutes with a solution containing, per 1000 parts, 0.5 part of a commercially available soaping agent based on carboxymethylated alkylene oxide addition product and then rinsed with warm water.

The resulting fabric is then treated at room temperature for 20 minutes with an aqueous liquor containing per 1000 parts 3 parts of the product obtained in Example 1. The liquor to goods ratio is 20:1. After drying, there is obtained a scarlett red dyeing having a good chlorine water fastness at 83° (measured according to SNV 195.828).

Similar good results are obtained when the after-treatment of the reactive dyeing is effected with the products of Examples 2 to 18 instead of the product of Example 1.

APPLICATION EXAMPLE B

Mercerised knitted cotton goods are dyed at 98° for 60 minutes with an aqueous dyebath containing 1% dyestuff C.I. Reactive Blue 79 (based on the dry weight of the goods) and, per 1000 parts, 60 parts sodium chloride, 15 parts calc. sodium carbonate and 1 part sodium

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n-nitrobenzenesulphonate. The liquor to goods ratio is 40:1.

After dyeing, the goods are thoroughly rinsed with warm and cold water. They are then soaped and rinsed as disclosed in Example A above. Thereafter the goods are treated at 98° for 20 minutes with an aqueous liquor containing per 1000 parts 1.5 parts of the compound of Example 13 (without ethyleneglycol) and 5 parts sodium trichloroacetate. The liquor to goods ratio is 20:1. After drying, a blue dyeing having an excellent fastness to chlorine water (according to SNV 195.822) is obtained. The chlorine water fastness is also good after two washings at 60° (according to SNV 195.813).

APPLICATION EXAMPLE C

Bleached knitted cotton goods are dyed at 40° for 60 minutes with an aqueous dyebath containing

0.33% dyestuff C.I. Reactive Orange 91	} based on the dry weight of the goods
0.40% dyestuff C.I. Reactive Red 184	
0.20% dyestuff C.I. Reactive Blue 184	
and, per 100 parts, 60 parts calc. sodium sulphate 1 part calc. sodium carbonate, and 2 parts (in volume) 36% sodium hydroxide.	

The liquor to goods ratio is 20:1.

The goods are then rinsed, soaped and after-treated as disclosed in Example B above.

The resulting beige dyeing has a good chlorine water fastness.

APPLICATION D

Bleached cotton fabric is dyed according to the procedure of Example A above but using the following dyestuffs:

6.4% dyestuff C.I. Reactive Yellow 25	} based on the dry weight of the goods.
3.5% dyestuff C.I. Reactive Red 147	
1.4% dyestuff C.I. Reactive Blue 193	

After rinsing, soaping and rinsing the goods are treated at 60° for 20 minutes with an aqueous liquor containing, per 1000 parts, 2 parts of the compound of Example 18. The liquor to goods ratio is 20:1.

The resulting dyeing has a very good chlorine water fastness at 83°. This property is still maintained after three successive washings with chlorine water.

Similar good results are obtained when the dyed substrate is padded with an aqueous liquor containing/1000 parts, 20 parts of the compound of Example 18, squeezed to 80% of the substrate dry weight and dried at 120°.

APPLICATION EXAMPLE E

Bleached cotton cretonne is dyed at 98° for 90 minutes with an aqueous dyebath containing 2% dyestuff C.I. Direct Red 207 based on the dry weight of the substrate and 15 parts calc. sodium sulphate per 1000 parts. The liquor to goods ratio is 20:1.

After thoroughly rinsing with cold water, the substrate is after-treated at 60° for 15 minutes with an aqueous liquor containing per 1000 parts 2 parts of the compound of Example 16 (without ethylene glycol) and then dried.

The resulting bordeaux dyeing exhibits a good chlorine water fastness.

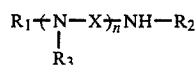
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The same good results are obtained when the substrate dyed with 3% dyestuff C.I. Direct Blue 199 is after-treated according to the same procedure.

By following the same procedure as indicated in Examples B-D but using the compounds of the other Examples, dyeings with good chlorine water fastness are obtained.

What is claimed is:

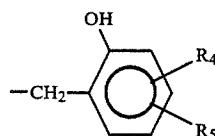
1. A compound of formula I



15 in which

R₁ is an aliphatic C₆₋₂₂ group

R₂ is a group of formula (a)



each R₃, independently, is hydrogen or a group of formula (a)

each R₄, independently, is hydrogen or C₁₋₁₂ alkyl
each R₅, independently, is hydrogen, chlorine, C₁₋₁₂ alkyl, cycloalkyl or phenyl

n is an integer from 1 to 10

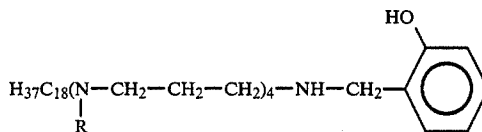
each X, independently, is —C₂H₄— or —C₃H₆—, provided that the molecule contains from 1 to 5 groups of formula (a), in free base, protonized or quaternized form.

2. A compound according to claim 1, in which R₄ and R₅ in the group of formula (a) are hydrogen.

3. A compound according to claim 1, in which R₁ is C₁₂₋₁₈-alkyl or C₁₂₋₁₈alkenyl, R₂ is salicyl, each R₃, independently, is hydrogen or salicyl, X is —CH₂H₆— and n is 1, 2, 3 or 4, the molecule containing 1, 3 or 4 salicyl groups.

4. A compound according to claim 1, in which R₁ is stearyl, cetyl or tallow fatty residue, R₂ is salicyl, X is —C₃H₆— and either n is 3 and R₃ is salicyl or n is 4 and one R₃ is hydrogen and the remaining R₃'s are each salicyl.

5. A compound according to claim 1, of formula



in which one R is hydrogen and the remaining R's are each salicyl.

6. A compound according to claim 1, in which when the compound is protonized or quaternized, the anion of such a form is halogenide, benzenesulphonate, p-toluenesulphonate, sulphate, methylsulphate, phosphate or formate.

7. A compound according to claim 1 wherein each R₁ is linear or branched C₆₋₂₂alkyl or C₆₋₂₂alkenyl, each R₄, independently, is hydrogen or C₁₋₄alkyl, and each R₅, independently, is hydrogen, chlorine, C₁₋₄alkyl, cyclohexyl or phenyl, provided that when R₄ is C₁₋₄al-

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kyl it is ortho or meta to the hydroxy and when R₅ is other than hydrogen it is para to the hydroxy.

- 8. A mixture of compounds according to claim 1.
- 9. A mixture of compounds according to claim 2.
- 10. A mixture of compounds according to claim 3.
- 11. A compound according to claim 3 in which, when

the compound is protonized or quarternized the anion is halogenide, benzenesulphonate, p-toluenesulphonate, sulphate, methylsulphate, phosphate or formate.

- 12. A mixture of compounds according to claim 4.
- 13. A mixture of compounds according to claim 7.

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